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EVALUATION OF THE ULTRAVIOLET-OZONE AND ULTRAVIOLET-OXIDANT TREATMENT OF PINK WATER

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Munitions wastes present some unique problems related to disposal or destruction, but are also similar to or representative of complex organic pollutants frequently encountered by the chemical industry. As such they offer an opportunity to evaluate new and novel technology for water pollution control. This report documents the investigation of two such innovative schemes for the destruction of such pollutants, presenting data on the effectiveness of three oxidants, ozone, hydrogen peroxide, and a proprietary peroxide salt when used in conjunciton with irradiation by ultraviolet light. The results of this study, in addition to being of direct interest to the military, will also be transferable to the control of a vast array of suspect pollutants encountered by the chemical industry. Development of such technology will assist industry in eliminating its chemical pollutants and meeting anticipated discharge requirements. For further information concerning this subject, the Industrial Pollution Control Division should be contacted.

David G. Stephan
Director
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Cincinnati

ABSTRACT

Pink water, a solution of trinitrotoluene (TNT) and other nitrobodies, is a major pollutant at ammunition plants engaged either in the manufacture of TNT or in the loading, assembly, and packing of bombs and shells. Purification of the water is currently accomplished by carbon adsorption at the more modernized installations where the carbon is used once and then burned; the result is a high cost operation and a potential air pollution problem. Although thermal regeneration of activated carbon with adsorbed explosives has been piloted, and appears to be cost effective, it has yet to be implemented at Army Ammunition Plants. As an alternative to carbon adsorption for the treatment of pink water, two new methods are reported here, the first involving the use of ultraviolet (uv)-ozone and the second using a uv-oxidant combination.

In the first study, a 3.79 cubic meters per day (m^3pd), equivalent to 1000 gallons per day (gpd), uv-ozone pilot system was evaluated. It was found that dissolved TNT and RDX were reduced to less than one milligram per liter (mg/L) with no by-products requiring disposal. A design for a 19 m^3pd (5000 gpd) pilot plant was proposed.

In the second study, a uv-oxidant process for treatment of pink water was examined. Commercially available uv water purification units in conjunction with an oxidant such as hydrogen peroxide or Oxone, (a blend of potassium persulfate oxidants), were evaluated for their efficiency in treating pink water. Variables such as film depth, dilution, uv wavelength, and operation of the units in series rather than in parallel were examined. A design for a 379 m^3pd (100,000 gpd) pink-water treatment plant was proposed.

This report is submitted by US ARRADCOM-DOVER, NJ (formerly Picatinny Arsenal) in fulfillment of Interagency Agreement D6-0059 with the US Environmental Protection Agency. The work was carried out during the period 6 June 76 to 30 Dec 77.

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All experimental work for the uv-ozone portion of this study was conducted by Westgate Research Corporation, West Los Angeles, California. The work performed on the uv-oxidant process was conducted by the Naval Weapons Support Center at Crane, Indiana.

SECTION 1

INTRODUCTION

Pink water is a unique pollutant which is generated from trinitrotoluene (TNT) manufacturing plants, and load, assemble, and pack (LAP) plants. Pink water also arises from unloading or demilitarization of munitions. Pink water from manufacturing operations may contain α-TNT, TNT isomers, and dinitrotoluenes (DNT). Pink water generated from LAP and demilitarization operations may contain α-TNT, cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), and wax.

The volumes and concentrations of pink water streams vary widely but, at full mobilization, volumes of 379 m^3pd (100,000 gpd) per line at concentrations of 100-150 ppm of TNT are not atypical. A complete review of TNT manufacturing and its wastes can be found in reference 1. Currently, activated carbon is the most widely used process for pink water abatement. The carbon is used once and then burned; the result is a high-cost operation and an air pollution problem. Although processes for thermal regeneration and reuse of carbon have been tried for the explosive laden carbon, all suffered from a high risk of explosion and a high loss of carbon. A new process for thermal regeneration of activated carbon, using a rotary kiln with a reducing atmosphere, has been piloted and appears to be safe and cost effective. However, it has yet to be implemented. Concurrent with thermal regeneration, new processes for abatement of pollution from pink water are also being investigated. This report describes the uv-ozone and uv-oxidant processes, two new technologies for the abatement of pink water discharges.

SECTION 2

CONCLUSIONS

UV-OZONE TREATMENT OF PINK WATER

Data obtained from a 3.79 m^3pd (1000 gpd) pilot plant demonstrated the feasibility of using uv-ozone to oxidize TNT and RDX in aqueous solution and produce an effluent containing less than 1 mg/L of TNT and RDX.

A design was proposed for a 19 m^3pd (5,000 gpd) modular uv-ozone pilot plant for treating pink water. The proposed design would allow a single unit to be used for low-flow applications, or multiples to be used in series for full mobilization requirements.

UV-OXIDANT TREATMENT OF PINK WATER

From the studies performed, using commercially available units for water purification via uv irradiation, the procedures incorporating Oxone* are more efficient than H_2O_2 in reducing the total organic carbon levels.

A design for a 379 m^3pd (100,000 gpd) uv-oxidant treatment plant was proposed.

* Oxone, a product of the DuPont Corporation, is a mixture of potassium monopersulfate, potassium hydrogen sulfate, and potassium sulfate.

SECTION 3

RECOMMENDATIONS

UV-OZONE TREATMENT OF PINK WATER

A 19 m^3pd (5000 gpd) pilot plant should be evaluated at an ammunition plant in order to determine the operating conditions required for achieving the minimum fixed and operating costs for a 379 m^3pd (100,000 gpd) plant.

An economic analysis should be performed on the 19 m^3pd (5000 gpd) unit after process parameters have been optimized.

UV-OXIDANT TREATMENT OF PINK WATER

Equipment should be found for the uv-oxidant process that would be suitable for purification of large volumes of pink water.

Further studies of the process should be made only if more cost-effective equipment is developed to process the volumes and concentrations of pink water to be expected in a full-scale plant.

SECTION 4

UV-OZONE TREATMENT OF PINK WATER

The objective of the uv-ozone testing was to develop design criteria and cost figures for a 379 m^3pd (100,000 gpd) pink-water treatment plant. Tests were made in a 1000 gpd uv-ozone reactor to estimate the conditions for minimum power demand and retention time required to obtain an effluent containing less than 1 mg/L of TNT and less than 1 mg/L of RDX.

DESCRIPTION OF ULTROX PILOT PLANT

This pilot plant, recently developed by the Westgate Research Corporation, is designed to demonstrate the practicality and cost effectiveness of UV-ozone oxidation for destroying organics in wastewater. The pilot plant can vary input and intensity of uv radiation, ozone mass transfer, mixing, and water flow rate. The reactor is fabricated from 304 stainless steel which is passivated and electropolished to reduce chemical attack and increase uv reflectivity. A separate NEMA cabinet houses the ballasts for the uv lamps.

The reactor can accommodate 30 low-pressure, 65 watt uv lamps and has six operating stages. From 0 to 30 lamps can be turned on in a test run. Ozone is uniformally diffused from the base of the reactor through spherical spargers that generate gas bubbles of 2.5 mm diameter. The number of spargers can be varied from stage to stage, so that the overall mass transfer of ozone can be changed as desired.

The reactor is designed for low-pressure operation (2 psig, maximum) to reduce the cost for pumping water and compressing air for ozone generation. Low-pressure operation not only provides greater safety but also reduces the thickness, weight, and cost of materials of construction. However, it reduces the effective oxidant concentration.

PILOT PLANT OPERATION

In each stage the water is contacted by the ozone and, in certain stages, uv radiation. The flow rate of the incoming pink water is measured by a rotameter located between the pump and the reactor inlet. The water is fed to the reactor by the use of a gear type, sealless, magnetic drive pump with integral, solid-state speed control. The flow of pink water through the reactor can be varied by this pump from 1.27×10^{-5} m^3/s to 1.27×10^{-4} m^3/s (0.2 to 2 gpm) with retention times varying from 37.5 to 375 minutes.

The purified water leaving the reactor overflows into a gas-water separator in order to eliminate entrainment of water in the exhaust gas, and then drains into a sump. No level controls are required within the reactor.

TEST PROCEDURES

From previous experience with pink water and waters of similar composition, it had been determined that the following variables have the greatest influence on total power demand, reactor size, and retention time:

1. concentration of O_3 in sparging gas
2. intensity of uv radiation
3. placement of uv lamps within reactor
4. temperature of incoming water flow rate
5. composition and concentration of solute

PRELIMINARY TESTING

Analysis provided by ARRADCOM showed that the pink water contained 140 mg/L TNT, 72 mg/L RDX, 10 mg/L wax and 68 mg/L of TOC. The synthetic pink water prepared for the shakedown tests was mixed to contain this concentration of TNT. An in-line filter was inserted at the inlet of the pilot plant to remove residual suspended solids. The results of experiments with the synthetic solution, shown in Table 1, helped to estimate the operating levels for the number of uv lamps per stage and the ozone mass flow required to treat actual pink water.

Table 1. UV-Ozone treatment of TNT in water

Test No.[d]	Total organic carbon (mg/L)[a]		
	Influent	Stages 1-3[b]	Stages 4-6[c]
1022	60	13	3.0
1023	55	7	2.5
1024	66	5	1.2
1025	66	5	2.0
1026	54	10	6.5

a. Based on a flow rate of 1200 ± 100 mg of ozone per minute.

b. 7 ± 2 W uv per mg TOC

c. 40 ± 20 W uv per mg TOC

d. Temperatures were about 30°C and residence time was 118 minutes.

PINK WATER TESTS

Results of pilot plant tests using ARRADCOM pink water are summarized in Table 2. The first test (No. 1027) was run at conditions similar to test No. 1026 for TNT in water. Greater resistance to oxidation was found when using pink water than TNT in water. Therefore, the residence time and number of uv lamps were increased in subsequent tests (1028 and 1029).

Table 3 shows a comparison of conditions and results for TNT in water and pink water in tests 1024 and 1029, respectively. The ozone to organic carbon ratios are about the same for the first three and the last three stages; however, the ratio of uv input power to carbon had to be increased in both the first three and second three stages in order to achieve 3 mg/L TOC after six stages for the pink water.

SPECIFIC ANALYSIS

Table 4 indicates that less than 1 mg/L TNT and 1 mg/L RDX remained in the effluent, but there was also some unidentified residue both with TNT in water and with pink water. Test No. 1029 indicated that the TNT and RDX levels were below 1 mg/L after the pink water had passed through the first three stages of the reactor. This result was most encouraging, since it means that the residence time, the number of uv lamps, and the ozone input can be reduced by half of the amounts used in test No. 1029.

DISCUSSION OF TEST RESULTS

The mass ratio of ozone to TOC in test No. 1029 for the first three stages was 13, which is 1.6 times the stoichiometric ratio for oxidation of carbon to CO_2. Bench and pilot plant tests on a wide variety of wastewaters have indicated that the minimum stoichiometric ratio of O_3 to TOC varies between 1.3 and 2.0, depending on the original TOC concentration and the chemical structure of the organic contaminants. (This calculation does not include hydrogen and nitrogen oxidation) Thus, pink water behaves in a manner similar to other wastewaters with dissolved organic matter.

Table 2. UV-Ozone treatment of ARRADCOM pink water

	Total Organic Carbon (mg/L)		
Test No.[e]	Influent	Stages 1-3[c]	Stages 4-6[d]
1027[a]	68	22.0	17.0
1028[b]	67	6.5	5.0
1029[b]	70	5.0	3.0

a. Residence time - 118 min.

b. Residence time - 177 min.

c. 1200 ± 100 mg ozone per min; 7 ± 2 W uv per mg TOC

d. 1200 ± 100 mg ozone per min; 40 ± 20 W uv per mg TOC

e. Temperature 29°-30°C in each test

Table 3. Comparison of synthetic and ARRADCOM pink water tests

Test No.	Ozone/TOC mass ratio (mg/mg)		Input, Watts/mg		TOC (mg/L)		
	Stages 1-3	stages 4-6	stages 1-3	stages 4-6	Influent	stage 3	stage 6
1024[a]	15	198	7	60	66	5	1.2
1029[b]	13	180	11	140	70	5	3

a. Synthetic sample

b. Pink water

Table 4. Analysis of synthetic and ARRADCOM pink water

Test No.	Sample	TNT (mg/L)	RDX (mg/L)	Residue (mg/L)
1020-1	Synthetic influent	76	-	-
1020-2	Synthetic effluent	<1	-	-
1023-2	Synthetic effluent	<1	-	11
1024-2	Synthetic effluent	<1	-	8
1025-2	Synthetic effluent	<1	-	6
1028-2	Pink water effluent	<1	<1	12
1029-1	Pink water effluent after stage 3	<1	<1	9
1029-2	Pink water effluent after stage 6	<1	<1	11

Another way to examine the total oxidation of TNT and RDX is from the following stoichiometric relationships:

TNT

$$C_6H_2CH_3(NO_2)_3 + 18\ O_3 \longrightarrow 7\ CO_2 + 3\ HNO_3 + 18\ O_2 + H_2O$$

RDX

$$C_3H_6N_3(NO_2)_3 + 18\ O_3 \longrightarrow 3\ CO_2 + 6\ HNO_3 + 18\ O_2$$

The pink water contained 140 mg/L TNT and 72 mg/L RDX. According to the above equations, the theoretical amount of ozone required per liter to carry out the complete oxidations is 813 mg. Since the testing found that 910 mg/L was required to obtain an acceptable effluent, the ratio of actual to stoichiometric ozone is 1.12:1 (or an ozone efficiency of 89.3%).

Although it was found that more uv lamps were required to oxidize the pink water than the solution of TNT in water, the number of lamps required per unit volume in each reaction stage has not been defined. Further tests will be required to establish the number of lamps that produce the optimum effect at least cost.

DESIGN OF 19 m^3/d (5,000 gpd) UV-OZONE PILOT PLANT

With the data obtained from the 3.8 m^3pd (1000 gpd) reactor, the following criteria were recommended for the 19 m^3pd (5000 gpd) pilot plant.

Design Parameters

Reactor volume	2.6 m^3 (675 gal)
Reactor dimensions (W x L x H)	0.9 x 1.8 x 1.5 m (0.3 x 6 x 5 ft)
Water flow rate	19 m^3pd (5,000 gpd)
O_3	17 kg/day (37.5 lb/day)
uv lamps (65 watts each)	144

Assembly

The major components of the pilot plant are:

(1) reactor assembly

(2) NEMA ballast enclosure

(3) ozone generator

Components 1 and 2 are assembled on one skid and component 3 is mounted on another skid.

The reactor, shown in figure 1, consists of a stainless steel tank with baffles, and a cover assembly made up of the reactor cover, ozone diffuser, uv lamps, and supporting structure.

Construction

The reactor tank is fabricated from 316 stainless steel sheet about 0.5 cm (3/16 in) thick. All parts are certified heliarc welded. A 10.2 cm (4 in) wide lip is welded to the top of the tank to form a gasket flange containing a groove to accommodate a Hypalon seal. The tank is mounted onto the metal skid by bolts.

Five baffles are located vertically to create six reaction stages. Water flows in an undulating path from stage to stage as shown in figure 2. The baffles are designed for easy removal to permit alteration of the number of reaction stages as desired.

The ozone inlet manifolds, lamp venting tubes, and lamp conduits are welded across the reactor and provide adequate horizontal stiffening. Vertical stiffening is achieved by 3 strips of stainless steel welded to the cover plate, the manifolds, the gas vent and the wiring conduits. A diagram of the proposed pilot system is shown in figure 3.

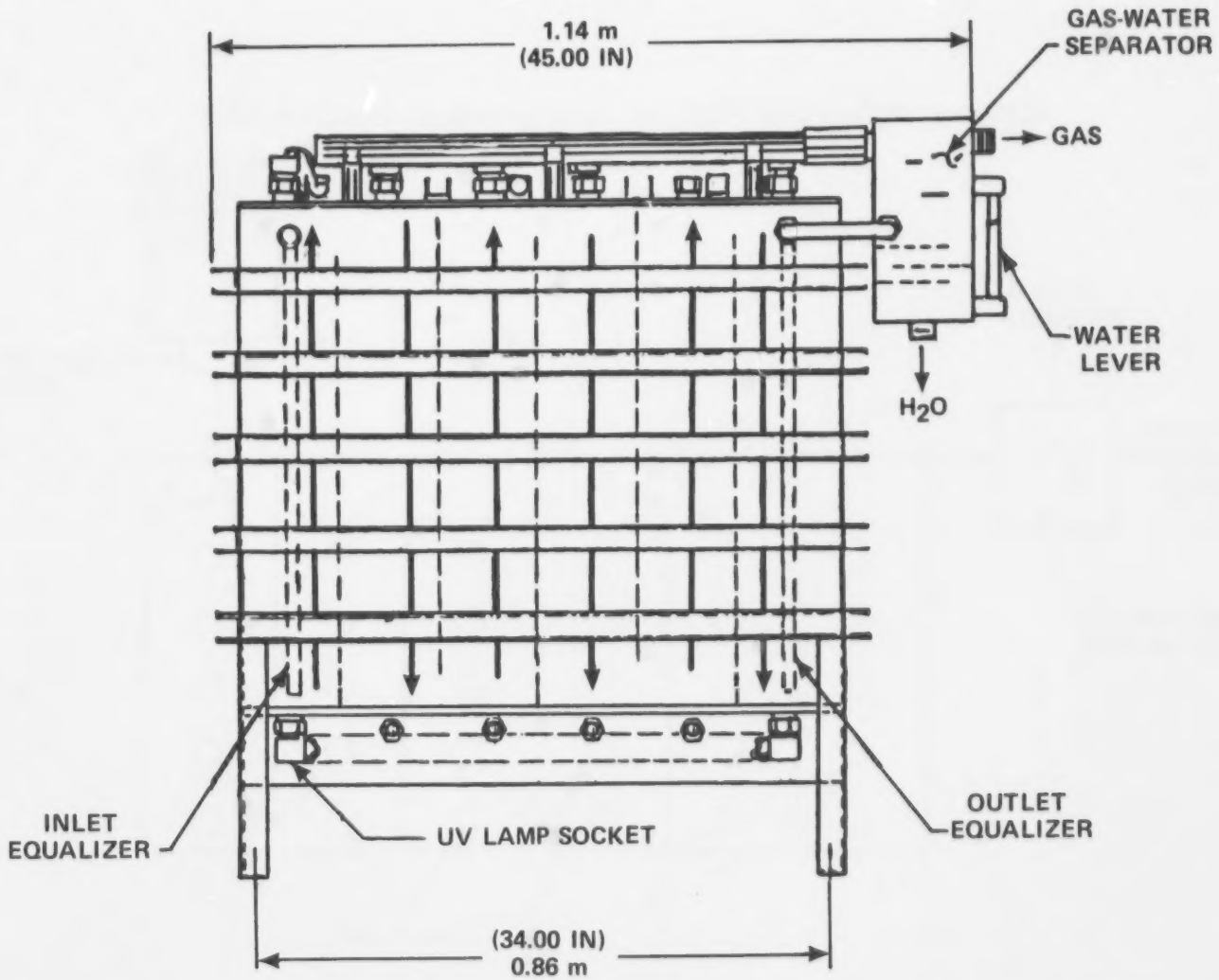

FIG 1. UV-OZONE REACTOR ASSEMBLY

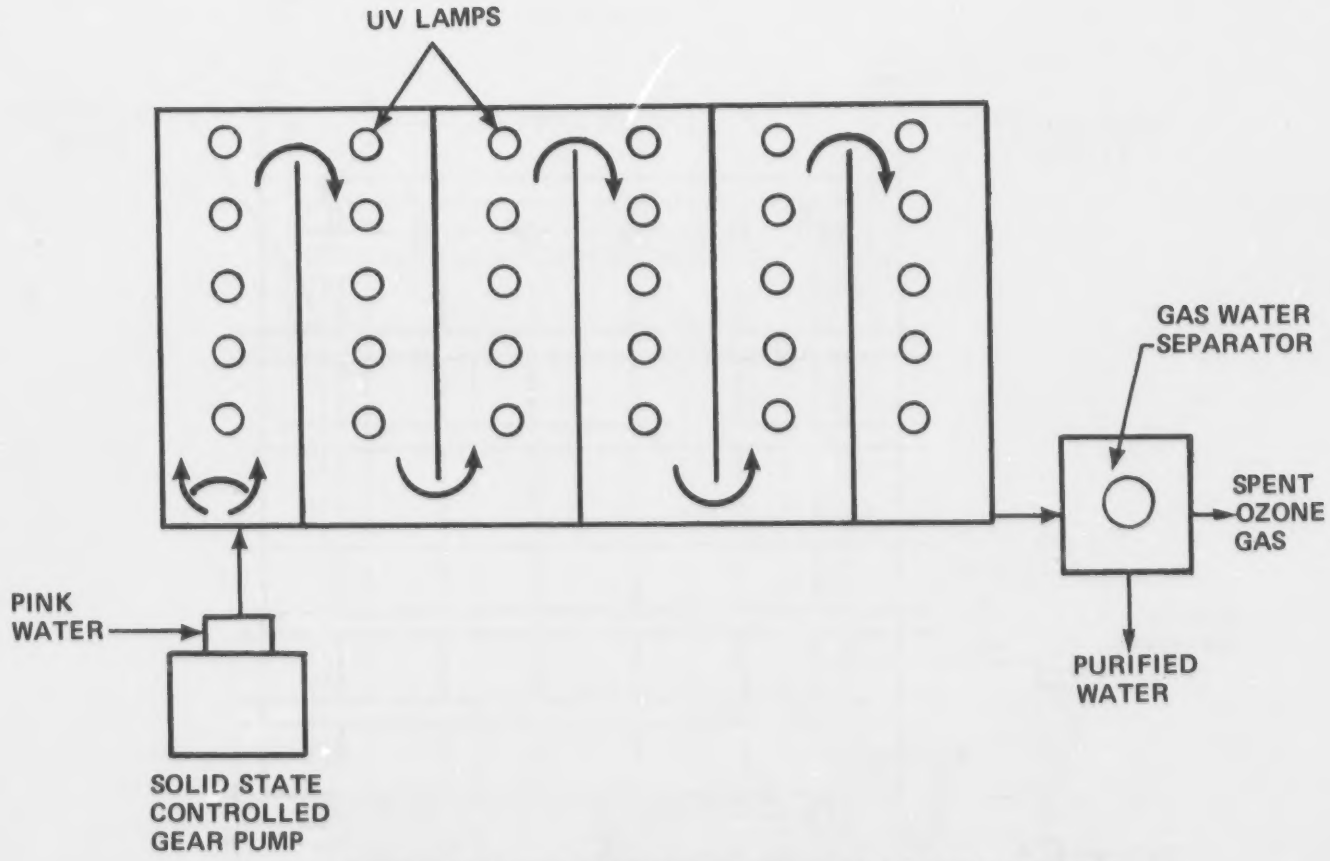

FIG 2. PATTERN OF WATER FLOW THROUGH PILOT PLANT REACTOR

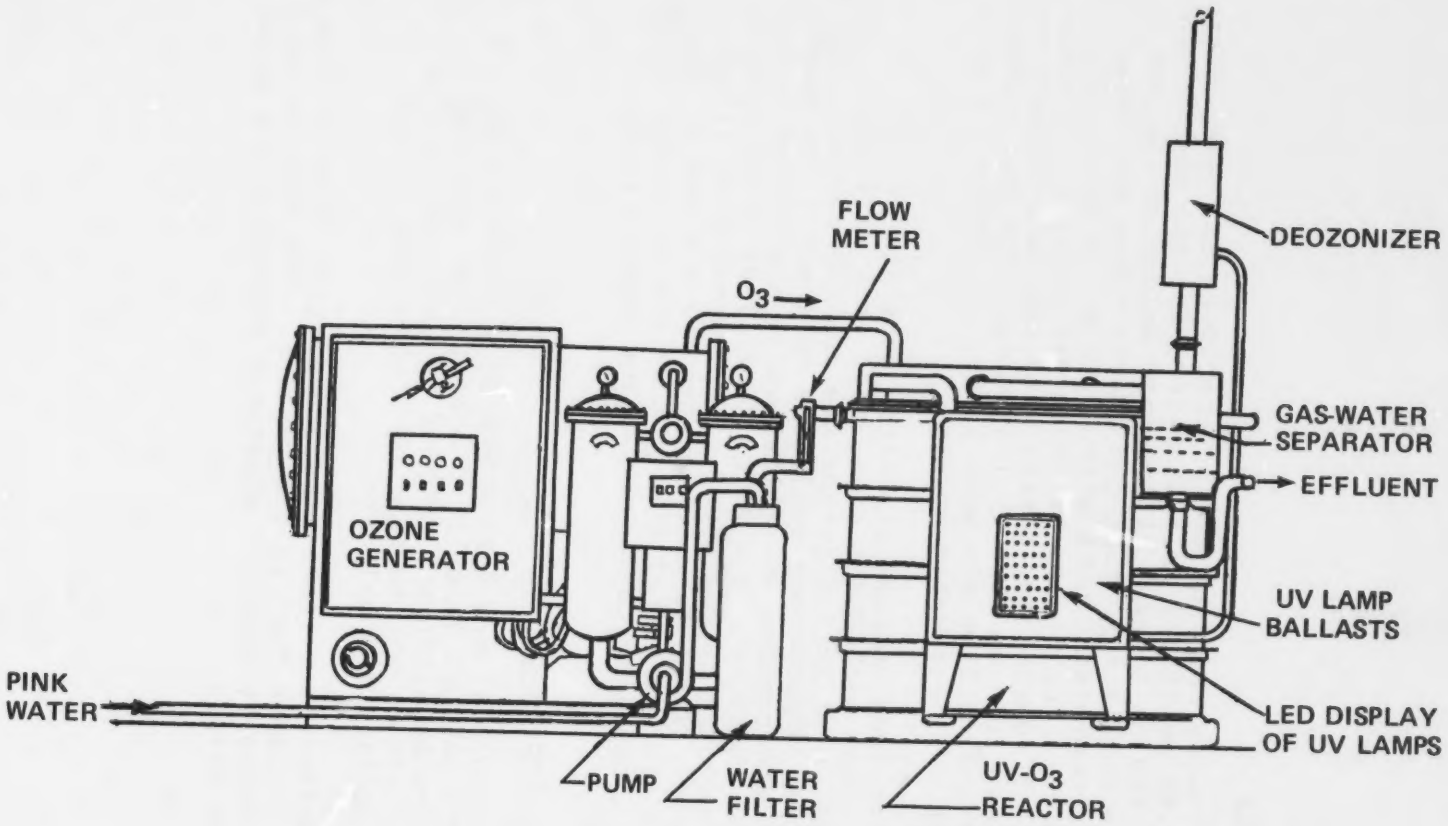

FIG 3. THE 920 M^3 PD (5000 GPD) PILOT PLANT ASSEMBLY

Cover Assembly

The following openings are punched into the cover plate: 144 holes, 2.86 cm (1 1/8 in.) diameter, for the quartz tubes that enclose the uv lamps. Nipples are welded at the top surface of these openings so that the quartz tubes are sealed to the cover by compression nuts with O-rings. 6 holes, 2.54 cm (1 in.) diameter, for the spent ozone gas outlets. 6 holes, 3.81 cm (1 in.) square, for mating with the lamp support structure. 6 holes, 1.59 cm (5/8 in.) diameter, for the outboard lamp support and cooling air vent lines. 2 nipples, 3.81 cm (1½ in.) with NPT, for water inlets.

The lower lamp support structure consists of 3.81 cm (1½ in.) square tubes with 0.159 cm (0.0625 in.) wall thickness. Holes of 2.54 cm (1 in.) diameter are drilled on the upper side of the tubes at appropriate positions to install the quartz tube support and sealing assemblies which are welded to the upper side of the tube. A 1.27 cm (½ in.) diameter hole is drilled through the outboard end of the conduit to attach the vent tube which also acts as a support for the end of the square tube. The center of the square tube is supported by welding the ozone line to the diffusers running parallel to the conduits.

NEMA Ballast Enclosure

A standard 1.52 m x 0.91 m x 0.31 m (5 ft x 3 ft x 1 ft), 16 gauge NEMA cabinet is used to contain and cool the 72 lamp ballasts. The ballasts are mounted on racks within the cabinet. A rotary air blower at the base of the cabinet directs the air upward for cooling the ballasts.

The cabinet door contains a LED display which indicates the number uv lamps "ON" in the reactor. The door is sealed to the NEMA housing by means of elastomer gasketing and spring-loaded screw clamps.

Ozone Generators

A number of manufacturers can supply generators which meet the 19 m^3pd (5,000 gpd) pilot plant requirement of 17 kg (37.5 lbs) of ozone per day. Manufacturers, such as OREC or PCI would supply two 9 kg (20 lb) per day ozone generators since neither produces an 18 kgs (40 pound) generator. The Welsbach generator is oversized but can produce 18 kg (40 lbs) per day efficiently by lowering the input voltage by means of a variable voltage transformer.

SECTION 6

UV-OXIDANT TREATMENT OF PINK WATER

Bench-scale studies have shown that short wavelength uv and H_2O_2 is very promising for the treatment of explosive contaminated effluents (2). This photo-oxidative treatment appears to be effective not only in decolorizing pink water, but also in destroying TNT, RDX, HMX, and other nitrobodies with a concurrent reduction in TOC concentration. These effects have been determined by gas, liquid, and thin-layer chromatography (GC, LC, TLC), total organic carbon (TOC), and C-14 labeled TNT assays.

DESCRIPTION OF UV-OXIDANT SYSTEM

A small-scale pilot system was used in which four uv water purification units were connected in series. These were Model 2000 units, manufactured by the Ultradynamics Corporation of Santa Monica, California, containing mercury vapor lamps (254 nm) protected by quartz jackets that are continuously cleaned by a hydraulically operated wiper assembly. The capacity of each chamber is approximately 22.8 liters (6 gallons). The maximum film depth is approximately 5.72 cm (2¼ in.).

Pink water from a bomb loading and steamout operation at Naval Weapon Support Center, Crane, Indiana was used in the study. Before being pumped into the system, the water was filtered to remove suspended solids which may interfere with the treatment. Because of the intense color, which would reduce the efficiency of the system, the pink water was diluted with tap water to yield the following results:

	Analysis, mg/L	
	1:1 Dilution	1:3 Dilution
TNT	70.9	34.1
RDX	72.4	27.0
HMX	9.4	4.1
TOC	52.6	27.0

From previous studies (2) it was found that 0.1% H_2O_2 is the optimum concentration to use in treating pink water. A 35% solution of H_2O_2 (Fisher Scientific Co.) was added to the pink water to be treated to yield a final concentration of 0.1% H_2O_2. The water was recycled from a reservoir through the uv units at a flow rate of 2.73 m^3/hr (720 gph) in a continuous flow mode. The actual residence time of the liquid in any one unit is about 0.5 minutes. A Model 500 unit (also manufactured by Ultradynamics Corp.) with a 2.54 cm (1 in.) film depth has been used to study the efficiency of the photo-oxidative treatment of pink water with respect to film depth. The capacity of its chamber is approximately 2.84 L (3/4 gal). One gallon of pink water (undiluted or diluted) containing 0.1% H_2O_2 was recirculated through the unit and back into a reservoir at a flow rate of approximately 0.4 m^3/h (105 gph).

PARAMETER VARIATIONS FOR OPTIMIZATION OF THE SYSTEM

Oxidizing Agents and Film Depth Studies

To test the effectiveness of a different oxidizing agent, a monopersulfate compound, Oxone (Dupont Chemical Co.), was substitured for the H_2O_2 in a number of studies. Overall efficiency was significantly increased by using 0.3% Oxone in place of 0.1% H_2O_2. Table 5 illustrates the results of treatment of a 1:3 diluted pink water solution in the UV 2000 (4 unit system) at a flow of 2.73 m^3/d (720 gpd), and in the UV 500 system at a flow rate of 0.4 m^3/h (105 gph) using either 0.1% H_2O_2 or 0.3% Oxone. The solutions were analyzed for wxplosives by liquid, gas, and thin-layer chromatography for dissolved organic matter by TOC.

From the results in table 5 it is evident that Oxone is far superior to H_2O_2. This can be seen with respect to decolorization time, TNT elimination, and degradation of polynitroaromatic by-products with corresponding reductions in TOC concentrations. Also illustrated by these results is that, with either oxidant, the 2.54 cm (1 in.) film depth of the UV 500 system enhances the efficiency of the treatment as compared with the 5.72 cm (2¼ in.) film depth of the UV 2000 system.

Studies were undertaken in which the concentration of Oxone employed in the treatment was varied. Additional studies were made to examine the potential of a combination H_2O_2/Oxone treatment. Because of the limited time available, it was only possible to examine the effects of using diluted pink water and 0.3% and 0.2% Oxone in the UV 2000 units, and 0.3% and 0.7% Oxone in the treatment of undiluted pink water in the UV 500 system. A combination of 01% H_2O_2 and 0.1% Oxone was also examined in the UV 2000 system. Table 6 illustrates the parameters and results of the treatment.

Table 5. Effects of Oxidant in the UV-2000 and UV-500 systems

System/Oxidant%	UV Exposure (hr)	Water analyses (mg/L) TNT	RDX	HMX	TOC*
UV-2000 0.1 H_2O_2	0.0	30.0	26.8	3.0	24.8
	3.0	0.01	0.01	0.02	5.6
	5.0	0.01	0.01	0.02	1.6
UV-2000 0.3 Oxone	0.0	34.0	27.4	2.8	24.2
	3.0	0.01	0.01	0.0	0.1
	5.0	0.01	0.01	0.02	0.2
UV-500 0.1 H_2O_2	0.0	29.0	20.6	3.1	23.0
	0.5	0.8	0.01	0.02	17.4
	1.5	0.05	0.01	0.02	8.0
UV-500 0.3 Oxone	0.0	29.0	20.6	3.1	23.0
	0.5	0.3	0.01	0.02	7.6
	1.5	0.01	0.01	0.02	1.8

* Includes other nitroaromatic compounds

Table 6. Effects of oxidant concentrations

Operating parameters			Original/Final analytical results (mg/L)			
Systems/ Oxidant	Dilutions	UV Exposure (hr)	TNT	RDX	HMX	TOC*
UV-2000 0.3% Oxone	1:4	3	28/0.01	26/0.01	27/0.02	22.8/0.3
UV-2000 0.3% Oxone	1:2	3	64/0.01	55/0.1	8.5/0.02	46.1/3.4
UV-2000 0.2% Oxone	1:4	3	23/0.01	19/0.01	2.4/0.02	21.8/0.4
UV-2000 0.1% Oxone, 0.1% H_2O_2	1:4	3	23/0.01	20/0.01	2.5/0.02	25.0/0.9
UV-500 0.7% Oxone	0	6	138/0.02	3.1/0.02	15.0/0.01	86.6/9.0
UV-500 0.3% Oxone	1:4	3	29.0/0.01	20.6/0.01	3.1/0.02	23.0/1.8

*Includes other nitroaromatic compounds

Treatment of 1:3 diluted pink water in the UV 2000 system with 0.3%, 0.2%, or 0.1% Oxone plus 0.1% H_2O_2 are comparable. The TOC levels were appreciably reduced, and no detectable amounts of explosives or polynitroaromatics were found after 3 hours of exposure. Treatment of an undiluted pink water solution with 0.7% Oxone in the UV 500 system is not as efficient as treatment of a 1:3 diluted pink water solution with 0.3% Oxone, but it is feasible if environmental trade-offs are allowed. The same is true of a 1:1 dilution of pink water treated in the UV 2000 system with 0.3% Oxone.

Flow Rates and Operations of Units In Series

Two flow rates were examined in the UV 2000 system. There appeared to be no major difference in results between flow rates of 2.04 and 2.73 m^3ph (540 and 720 gph) while operating in a continuous flow mode. If the ultimate treatment will be a direct passage, and not a recirculation of the pink water through the UV system, the flow rate will not be critical, but the total UV exposure time or contact time of the solution in the units will be. Operation in a continuous flow mode through 1 to 4 UV 2000 units in series appeared to have no major effect on overall efficiency as is seen in Table 7. This table illustrates the results of treatmentof a 1:3 dilution of pink water solution with 0.1% H_2O_2 through 1 to 4 units in series mode.

It would be extremely difficult to determine the overall effect of units in series with just 4 units operating in a continuous flow mode with the small volumes used. It is hypothesized that as the color of the solution disappears, the efficiency of the system increases because there is no loss of energy by color absorption. This can be demonstrated by diluting the pink water and examining TOC reduction per unit time. Table 8 illustrates the results of dilution studies. There is a decrease of 91% in the TOC level of the pink water after 3 hours of exposure in the UV 2000 system when the pink water is diluted 1:7 but only a 38% decrease with a 1:1 dilution. The relationship among these dilutions and the decrease in TOC observed after the exposure period appears to be linear, as illustrated in Figure 4. These results confirm the hypothesis that the process increases in efficiency with a decrease in color.

Comparison of Effect of Wavelengths

Aliquots of undiluted pink water containing 0.1% H_2O_2 were exposed to radiation of either 254 or 375 nm, in static modes, to determine if the wavelength had an effect on the destruction of explosives and a reduction in TOC. The film depth was 40 nm, with 30 minutes of radiation. After the irradiation at 254 nm, the pink water was completely decolorized and the TOC had de-

Table 7. Evaluation of UV-2000 system in series mode

Parameters [a]		Explosives content (mg/L)			
Units (No.)	Exposure (hr)	TNT	RDX	HMX	TOC [b]
1	5	<0.01	<0.01	<0.01	14.5
2	5	<0.01	<0.01	<0.01	4.4
3	5	<0.01	<0.01	<0.02	5.0
4	5	<0.01	<0.05	<0.05	2.5

[a] Pink water diluted 1:4, and treated with 0.1% H_2O_2 used in all tests.

b Includes other nitroaromatics

Table 8. Configurations for pink water pilot plant

Parameters			Analyses, mg/L (Original/Final)			
Dilution/ UV hrs	Volume m^3pd (gpd)	Oxidant	TNT	RDX	HMX	TOC
1:4/3	76 (20,000)	0.3% Oxone	28/ **	26/**	27/**	23/0.3
1:2/3	38 (10,000)	0.3% Oxone	64/**	55/**	5/**	46/3.4
1:4/3	76 (20,000)	0.2% Oxone	23/**	19/**	4/**	22/0.4
1:4/3	76 (20,000)	0.1% Oxone + 0.1% H_2O_2	23/**	20/**	5/**	25/0.9
1:4/5	76 (20,000)	0.1% H_2O_2	30/**	27/**	0/**	23/1.6
1:2/5	38 (10,000)	0.1% H_2O_2	64/**	48/**	9/**	45/13

* Includes other nitroaromatics

** < 0.05

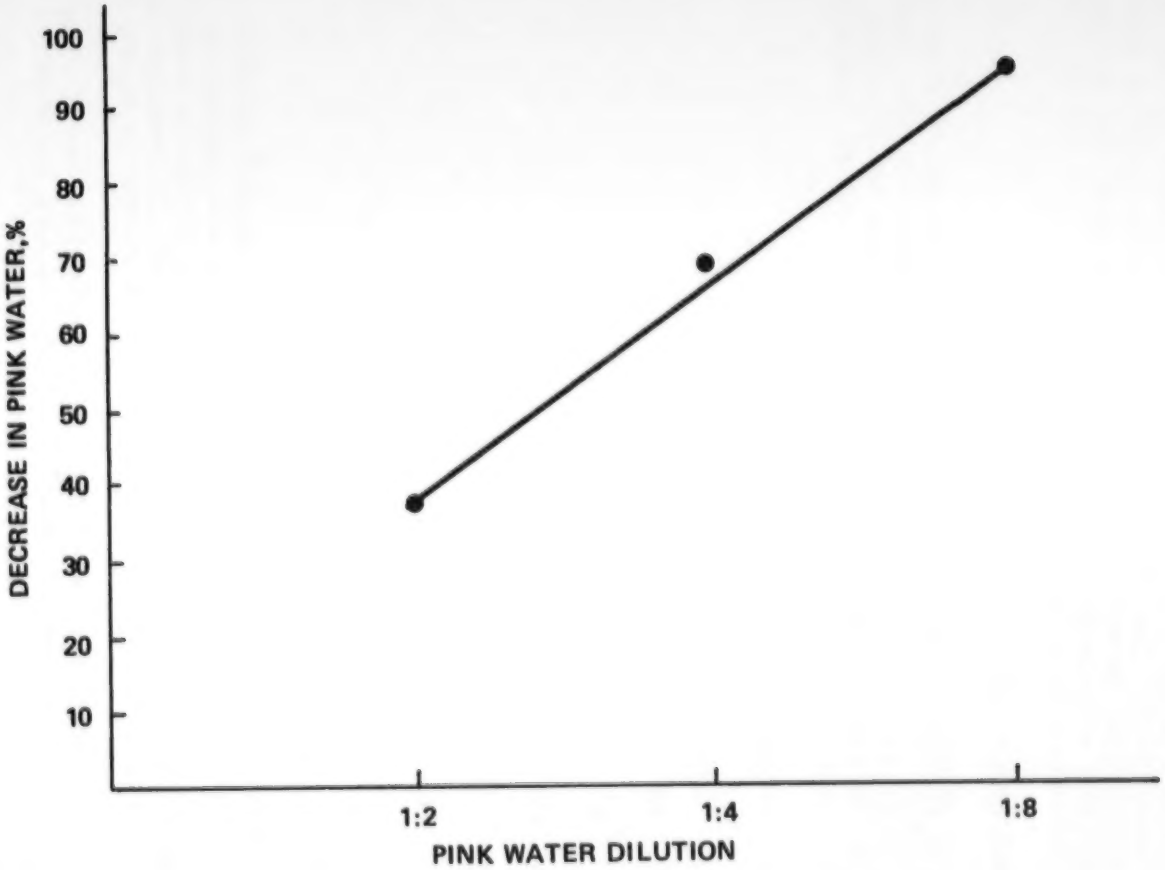

FIG 4. EFFECT OF DILUTION ON TOC REDUCTION IN PINK WATER AFTER 3 HOURS IN UV-2000 APPARATUS

creased from 89 mg/L to 9 mg/L. On the other hand, the color of the solution exposed at 375 nm was intensified, and no loss of TOC was noted. However, the TNT level in the pink water dropped to 0.02 mg/L after exposure at 375 nm but only to 0.15 mg/L after exposure at 254 nm indicating that the higher wavelength uv-light can alter the TNT molecule but cannot oxidize it. The significant reduction of TOC and rapid decolorization observed with the sample irradiated at 254 nm is a good indication that this shorter wavelength has a pronounced effect on overall efficiency of the photo-oxidation system.

CHEMICAL REACTIONS

The proposed oxidation mechanism is the production of free OH radicals which are ultimately responsible for the destruction of the explosives in the water upon exposure to uv light. The reaction mechanisms are represented below with RH representing the explosive.

a. Peroxide mechanism

$$H_2O_2 \longrightarrow 2 \cdot OH$$

$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$

$$R\cdot \xrightarrow{uv} \text{cleavage of ring}$$

b. Persulfate mechanism

$$HOOSO_3^- \longrightarrow \cdot OH + \cdot OSO_3$$

$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$

$$R\cdot \xrightarrow{uv} \text{cleavage of ring}$$

ADDITIONAL ANALYSES

In addition to explosives analyses, treated samples with high TOC levels (2 mg/L) were analyzed for nitrosoamines and sulfonates. No detectable levels of these products could be found by TLC procedures (sensitivity 50 ppb) in samples irradiated in the UV 2000 or UV 500 system with either H_2O_2 or Oxone.

In all treatments with H_2O_2, the peroxide level also was monitored. The range of residual peroxide was between 30 and 100 ppm after 3 or 5 hours of exposure in the UV-2000 system and 1.5 hour in the UV-500 system.

The pH of the pink water solutions containing H_2O_2 or Oxone was monitored before and after treatment. Before treatment, the pH values averaged 7.3 and 3.2, respectively. After treatment, the values fell to 6.4 and 2.4. If the extremely low pH of the

water treated with Oxone poses a problem, it can be economically and simply neutralized by the addition of lime after treatment and before discharge.

Design Parameters of Full-Scale UV-Oxidant System

If pink water is to be treated effectively it must be filtered to remove suspended solids before irradiation. The separated explosive crystals could be reclaimed, if desired.

After eliminating the suspended solids, the liquid is diluted, if necessary, and pumped into a mixing tank where metered additions of hydrogen peroxide or Oxone are made. To be certain that a homogeneous solution is prepared, the pink water and oxidant are further mixed by an in-line triblender after which the mixture is pumped into the UV-system for treatment. Figure 5 illustrates the general design of the system. After treatment, the water can be discharged directly into a sewer line or, if H_2O_2 was used as the oxidizer, the water can be recycled for dilution of additional pink water. Recycling of the treated water originally containing Oxone is not allowable without further treatment since residual amounts of potassium and sulfate ions in the treated water would increase with each fresh addition of Oxone.

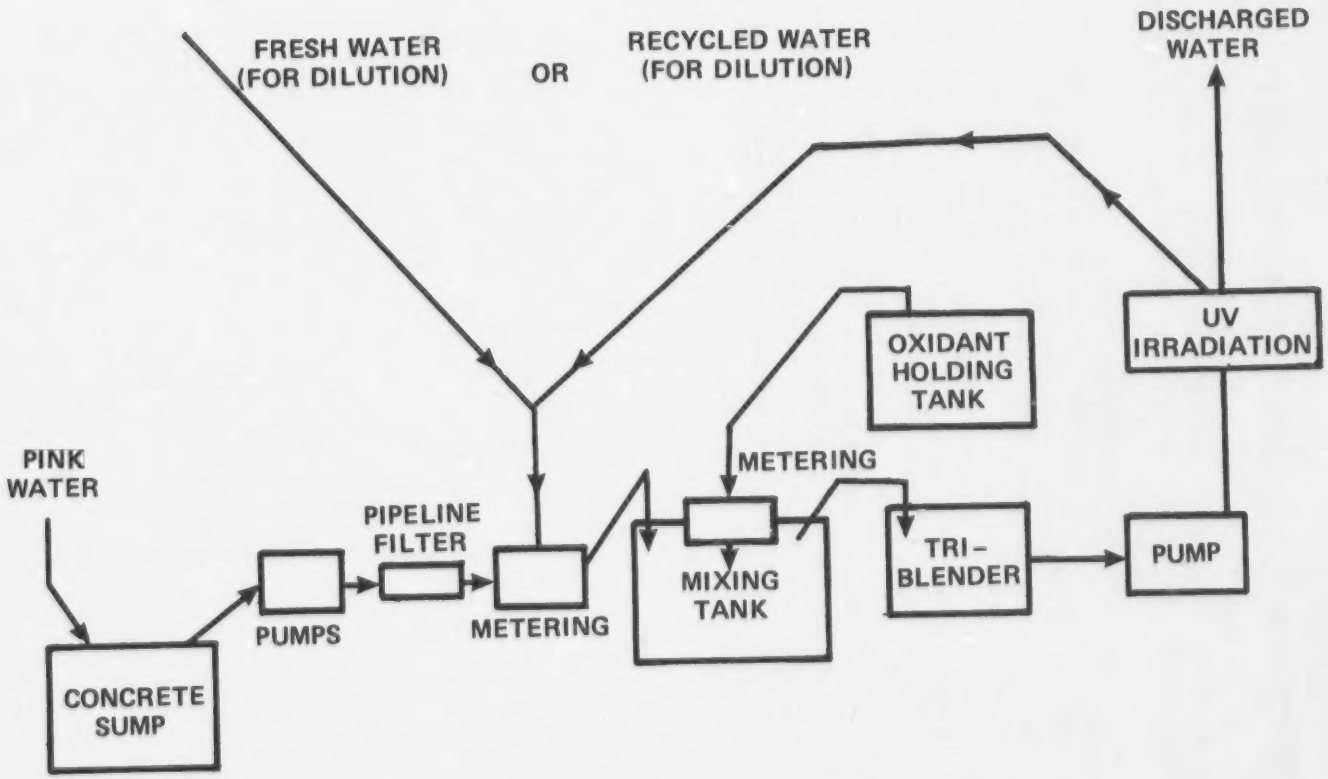

FIG 5. BASIC DESIGN OF THE UV-OXIDANT SYSTEM

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